6^{th} Quarterly Status Report
Liquid-Phase Deposition of α-CIS Thin Layers
Contract # XDJ-3-30630-33

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August 12, 2004

Since the submission of our last quarterly status report, we have made significant advances in the area of TEM sample preparation and in characterization of deposited Cu–In–Se films via TEM. In this report we will show that we have successfully deposited a thin layer with coarse grain sizes of α-CIS. Additionally, we have established the capability to perform substrate etching prior to deposition within the sliding boat reactor.

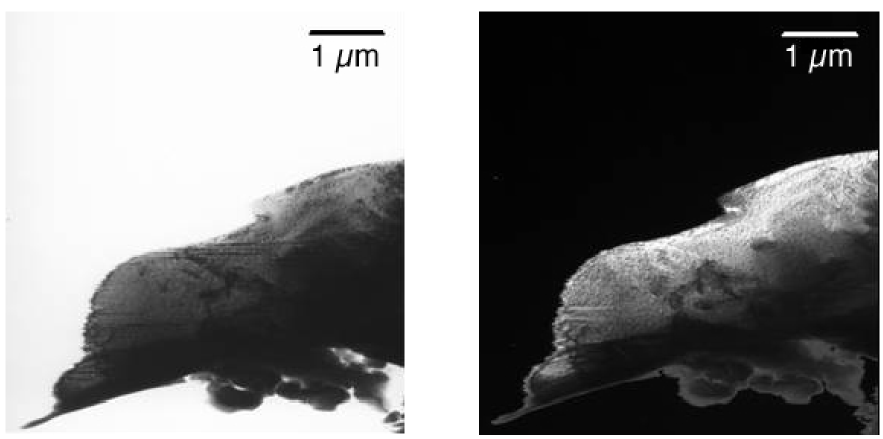

Figure 1: Bright field image on left (dark field on right) revealing course grain of deposited α-CIS.

Grain Size

Figure 1 presents bright-field and dark-field TEM images of deposited films containing α-CIS. In both images, regions of constant crystal orientations show up with the same gray level (dark

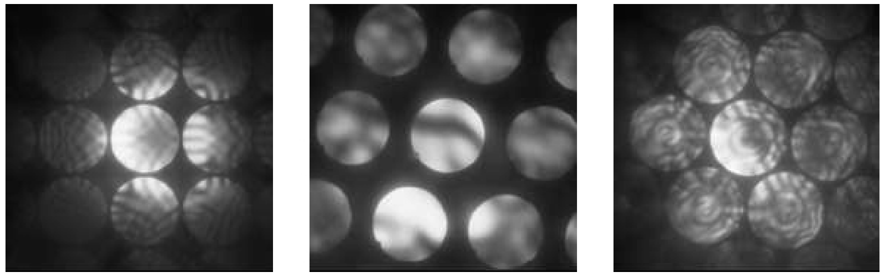

Figure 2: CBED patterns from 110, 110, and 112 zone axis orientations.

in the bright-field image and bright in the dark-field image). From Fig. 1, it can be clearly seen that grains sizes within the deposited films exceed several micrometers. The demonstration this capability of liquid-phase deposition to provide films with a very large grain size constitutes an important mile stone of our project. Selected-area electron diffraction (SAED) patterns where obtained from the grain in Fig. 1 in zone axis orientations of $\langle 001\rangle$, $\langle 110\rangle$, and $\langle 112\rangle$. The patterns display only one lattice of spots, confirming the existence of only one grain within the region of interest, and match simulated SAED patterns we have obtained with the help of the JAVA Electron Microscopy Simulation software package "JEMS" (P. Stadelmann, EPFL, Lausanne) to within only $1\,\%$ deviation, both azimuthal and radial.

We need to point out, however, that these diffraction patterns alone are not sufficient to conclusively *prove* the existence of α-CIS. This is due to the fact that many phases of Cu–In–Se, and in particular those that were identified in the compositional neighborhood of α-CIS, also possess tetragonal crystal lattices with lattice parameters very close to those of α-CIS. This circumstance makes it difficult to determine the phase of the deposited material by X-ray or conventional electron diffraction alone.

On the hand, simulated Convergent Beam Electron Diffraction (CBED) patterns of the phases in question should reveal distinct differences in the fine detail, namely the pattern of the higher-order Laue zone (HOLZ) lines, thus enabling us to discern α-CIS from undesired phases. Initial CBED patterns we obtained from the grain in Fig. 1 are shown in Fig. 2. However, these patterns merely exhibit Bragg fringes, and not the required HOLZ lines. Accordingly, the quality of the TEM specimen as well as the CBED technique need further improvement.

Since we could not observe HOLZ lines yet, we determined composition of the film from which the TEM specimen of Figs. 1 and 2 was prepared by X-ray energy dispersive spectroscopy (XEDS) in the SEM. The ratio of Cu:In:Se atoms was found to be 24:30:46. Along with the SAED patterns, this is strong evidence – although not a proof – for the existence of α-CIS.

Substrate Etching

To grow well-adherent, uniform films of a single phase, it is imperative to have a substrate that is free of contaminants. Currently, we are setting up the ability to etch substrates by two separate methods. First, an etch-back can be achieved with the use of the sliding boat (described in previous reports), which contains two separate reservoirs. Loading one reservoir with the *substrate* material, contact with the substrate will cause atoms at the substrate surface to dissolve into the reservoir, thus exposing a contaminant-free surface. An obstacle to this approach is that it requires choosing a substrate with a proper work function to form an ohmic contact with α-CIS, and at the same time must enable sufficiently high diffusivity at the deposition temperature.

Our second approach involves the use of a gas mixture containing an inert gas and hydrogen. After evacuating the deposition chamber and backfilling with argon several times, almost all of the oxygen can be removed from the chamber. However, even after this is completed, there still remain oxides on the surface of the substrate material. The hydrogen can reduce theses oxides and to form the water, which can then be removed by the pumps attached to the growth reactor.